

Article

Biodiesel from Rapeseed and Sunflower Oil: Effect of the Transesterification Conditions and Oxidation Stability

Elena Khan ¹, Kadir Ozaltin ² , Damiano Spagnuolo ³ , Andres Bernal-Ballen ⁴, Maxim V. Piskunov ⁵ 
and Antonio Di Martino ^{1,*} 

¹ Research School of Chemistry & Applied Biomedical Sciences, Tomsk Polytechnic University, Lenin Avenue 43, Tomsk 63400, Russia

² Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Nam. T.G.M. 5555, 76001 Zlin, Czech Republic

³ Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Salita Sperone 31, 98166 Messina, Italy

⁴ Facultad de Educación, Grupo de investigación Conciencia, Universidad Antonio Nariño, Calle 22 sur No. 12D-81, Bogota 111821, Colombia

⁵ Heat Mass Transfer Laboratory, Tomsk Polytechnic University, Lenin Avenue 43, Tomsk 63400, Russia

* Correspondence: dimartino@tpu.ru

Abstract: In this study, we produced biodiesel fuel from two vegetal sources, rapeseed oil and sunflower oil, by transesterification reaction. The study aims to evaluate the impact of type of alcohol, its concentration and the reaction time, while keeping constant the temperature and the catalyst on the yield and quality of the biodiesel. For alcohol, methanol and ethanol were used at a molar ratio with the oil from 3 to 24. Transesterification was performed at various reaction times; 20, 40, 60 and 90 min for each oil and defined alcohol:oil molar ratio. The influence of these parameters on the biodiesel yield and properties were investigated in terms of density, viscosity, heating value, flash point, elemental content, density and oxidative stability of the final product. The benefit of oxidation stabilizers, catechol and 4-allyl-2,6-dimethoxyphenol was investigated. Results demonstrate that for rapeseed oil, the optimum reaction conditions to obtain a higher yield and quality of biodiesel were an alcohol:oil molar ratio of 15:1, with 60-min reaction time at 50 °C; while in the case of sunflower oil, the best yield and biodiesel quality were at an 18:1 molar ratio, with a 40-min reaction time and at 50 °C. In both cases, methanol provides the highest yields of biodiesel, and the obtained products satisfy the required standards and present a similarity with mineral diesel tested in same conditions.

Keywords: biofuel; rapeseed oil; sunflower oil; transesterification; catechol; 4-allyl-2,6-dimethoxyphenol



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1. Introduction

Energy represents a key source for economic growth, and since their discovery, fossil fuels have been the major contributor to fulfilling energy needs [1]. However, due to environmental issues related to the overuse and combustion of these fuels, together with the increase in price and depletion of natural energy, sources have forced researchers to find cost-effective, sustainable, renewable and efficient alternative energy sources [2]. To date, several renewable sources, including water, wind, geothermal and biofuels have been explored to reduce the use of fossil fuels, as well as their environmental impact caused by emissions of greenhouse gases.

Biodiesel is an environmentally friendly energy source, due to lower direct and indirect greenhouse gas emissions compared to fossil fuels [3]. The adoption of biodiesel can definitely help to preserve the ecological balance compared to fossil fuels. Biodiesel is mainly produced by four approaches: blending of oils; pyrolysis (thermal cracking); microemulsion; and transesterification [4]. Among these, transesterification is considered the best economical technology, due to the operative conditions at low pressure and temperature and maximum product yield [5].

By the transesterification reaction, biodiesel is obtained by mixing alcohol with raw materials containing triglycerides such as vegetable oil, animal fat, algae or recycling cooking oil. In the presence of a catalyst, the triglycerides react with alcohol forming fatty acid alkyl ester (biodiesel) as the main component, and glycerol, which represents a by-product [4–7]. The transesterification aims to reduce the viscosity of the vegetal oil [4]. Although the procedure is simple from the chemical points of view, it is difficult to conduct it properly, and in addition, the obtained biodiesel must adhere to the international standard. There are many parameters in the production of biodiesel, such as the type and concentration of catalyst, the alcohol and its molar ratio with oil, together with the temperature and the reaction time [8,9]. Among all of these, the nature of alcohol and the molar ratio of alcohol:oil are the variable, which mostly affect the yield and the final properties of the biodiesel [10].

Among the different alcohols used in the transesterification process, methanol and ethanol are favored when vegetable oils are used as feed-stock. Methanol is generally the primary choice, due to its quick and efficient reaction with triglycerides, and its molar structure reduces the steric hindrance, which is responsible for a low biodiesel yield [11]. Compared to methanol, ethanol has a higher cost and less reactivity due to the formation of azeotrope with water, causing uneasy recovery [12]. However, interest in using ethanol from biological sources is growing, in order to make the full process be considered as bio-based and renewable, even if the ethanol reactivity is strongly related to the feedstock and the reaction conditions [12,13].

The amount of alcohol in the transesterification, expressed in terms of the molar ratio of alcohol to triglycerides, is a key variable that has a direct impact on the reaction yield, quality and cost of the final product [14]. It is well known that in transesterification, three moles are of alcohol, three moles are obtained from fatty acids and one from glycerol. Due to the reversibility of the reaction, the alcohol to triglycerides molar ratio has to be higher compared to the stoichiometric ratio, in order to enhance the miscibility and the interaction between the alcoholic and the oil phase [12]. Generally, the molar ratio falls in the range from 6:1 to 30:1, depending on the type of oil and alcohol used and its source [15–19]. Defining the optimal molar ratio is highly important, as the content of alcohol influences the glycerol solubility within the ester phase, reducing the biodiesel yield due to the shift of the reaction towards the reagent type [15].

The reaction time represents another important parameter to set, as the conversion rate increases gradually over time, even if a prolonged time decreases the final production yield due to the reversibility of the reaction. As reported in [17], the reaction time falls between 20 min and up to several hours, according to the catalyst, volumes and types of alcohol and oil used. Generally, with base catalysts, the maximum yield is reached within 2 h, while a longer time is required for acid catalyzers due to their lower reactivity [20].

Another parameter to control during the transesterification is the temperature, as it directly affects the reaction rate; a higher temperature and reaction rate means a higher yield. However, the temperature should be lower than the boiling point of the alcohol, to avoid its loss and minimize the soap formation, which has a negative impact on the final yield. Depending on the type of alcohol, methanol or ethanol, the reaction temperature is set between 50 and 70 °C [17,21].

To obtain an efficient conversion rate, the transesterification requires the use of a catalyst; either homogeneous or heterogeneous acid or base catalysts are used. In homogeneous catalysts, soap formation, corrosion of reactor components and recovery issues are the recurrent drawbacks. Conversely, heterogeneous catalysts are non-corrosive and environmentally friendly, and can be easily separated from the products [22]. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the heterogeneous catalysts mostly adopted in the transesterification process from vegetal oils [23].

Considering what has been reported above, the reaction parameters such as the nature of the catalyst, time and temperature are parameters that can be easily monitored in the biodiesel production process. However, the alcohol to oil molar ratio and the type of alcohol

still seem to be the major challenges with the transesterification of vegetable oil, despite the many studies that have been reported. Their optimization is relatively complicated, due to their impact on the performance of the produced biodiesel as fuel. Therefore, to establish the optimal reaction, we set up conditions that can be easily applied to the large-scale production of biodiesel.

The aim of the presented experimental work is to evaluate and find out the convenient operation conditions in the transesterification of rapeseed and sunflower oil, and their influence on the obtained biodiesel properties. In particular, the interest is to define the differences between methanol and ethanol, the molar ratio the alcohol to oil and the reaction time, keeping the catalyst type, its concentration and the temperature constant. The influence of variation in those parameters on the biodiesel yield and quality is the goal of the work.

Oxidation stability and the effect of two oxidation stabilizers, 4-allyl-2,6-dimethoxyphenol and catechol, were also investigated.

2. Materials and Methods

2.1. Materials

For the biodiesel production, refined rapeseed oil and sunflower oil were provided by local producers. The reagents used for the transesterification and purification steps were as follows: methanol (99.9%); and potassium hydroxide (95%). For doping the two biodiesels, two antioxidants were used: catechol (>99% CAS 120-80-9); and 4-allyl-2,6-dimethoxyphenol (90% CAS 6627-88-9). These were purchased from Sigma–Aldrich (Moscow, Russia).

2.2. Biodiesel Preparation

The biodiesel from rapeseed oil and sunflower oil was obtained by transesterification reaction using homogeneous catalysts, as it represents a convenient and well-known approach. In brief, 200 g of each oil was preheated at 120 °C for 30 min under stirring to remove the moisture, and then transferred to a 500 mL glass flask. Afterwards, the solution containing alcohol (methanol or ethanol) and the catalyst (KOH) was prepared. For 50 mL of alcohol, 2 g of catalyst was used. The obtained methoxide/ethoxide solution was poured onto the oil, and the reaction was left to run at 50 °C for an established time. The alcohol concentration represents one of the variables evaluated. Samples at the following alcohol:oil molar ratio were prepared: 3:1, 6:1, 9:1, 12:1, 15:1; 18:1, 21:1 and 24:1 for both oils used. The second variable was the reaction time, wherein 4 intervals were evaluated: 20 min; 40 min; 60 min; and 90 min.

The parameters kept constant for each experiment were the KOH content (2 g for each 50 mL of alcohol); the temperature (50 °C); and stirring speed (700 rpm).

After the completion of the reaction, the two phases were left to separate by gravity, and the biodiesel separated from the glycerol, washed one time with aqueous acetic acid solution (1% *v/v*) and three times with distilled water to remove unreacted catalysts, soap and other side products. After the last washing with distilled water, the biodiesel was kept at 120 °C for 30 min to remove the residual moisture.

The impact of the reaction time and the alcohol:oil molar ratio on the biodiesel yield was calculated using the following equation

$$Y(g) = \frac{m_b}{m_o} \quad (1)$$

where *Y* represents the yield (g), while *m_b* and *m_o* the mass (g) of biodiesel and oil, respectively.

The preparation scheme is reported in Figure 1.

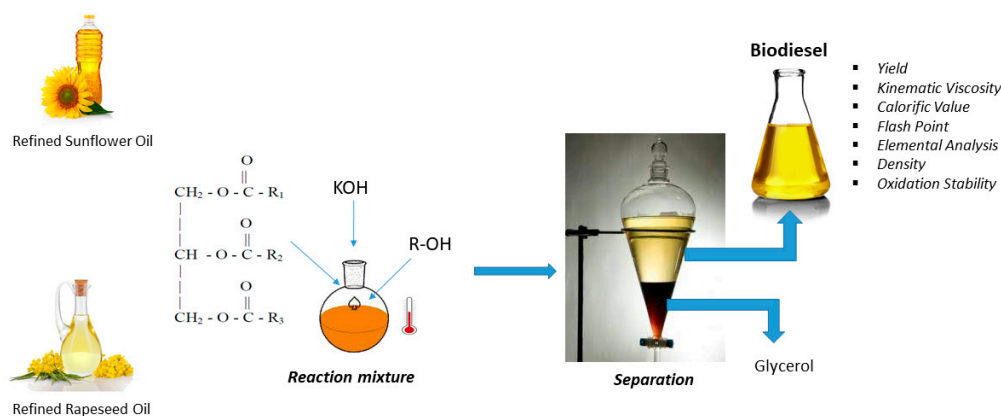


Figure 1. Schematic illustration of the biodiesel production process by transesterification and the parameters for the process and biodiesel characterization. KOH (potassium oxide); R-OH (alcohol).

2.3. Characterization and Quality Evaluation

The impact of the reaction time, type of alcohol and molar ratio (alcohol:oil) on the following final product yield, kinematic viscosity, calorific value, flash point, elemental analysis, density and oxidation stability, were investigated.

2.3.1. Kinematic Viscosity

The dynamic viscosity was determined by Anton-Paar MCR 502 at 40 °C. Three shear rates were used, specifically 7.5 s⁻¹; 15 s⁻¹ and 37 s⁻¹ following the ATSM D445 standard. Each measurement was performed in triplicate.

From the dynamic viscosity, the kinematic viscosity was calculated by the following equation

$$v = \frac{\eta}{\rho} \quad (2)$$

where v , η , ρ , are the kinematic viscosity (m²/s), the fluid density (Kg/m³) and the dynamic viscosity (Pa·s), respectively.

2.3.2. The Higher Heating Value Measurement

The Higher Heating Value (HHV) was measured by oxygen bomb calorimeter following the ASTM D240-14 standard. The calorimeter was calibrated using benzoic acid at 20 °C [24].

2.3.3. Flash Point

The flash point, is an indicator of the remaining methanol and the capacities of handling, storage and safety [25]. The Europea Standard (EN 14214) sets the flash point at 101 °C and the American Standard Testing Materials ASTM D6751-09 at 93 °C. The flash point was measured with a Pensky–Martens closed-cup apparatus using pure biodiesel and biodiesel in a blend with diesel.

2.3.4. Density

The biodiesel density influences the performance of pumps in fuel systems. The biodiesel density was measured following the EN ISO (International Organization for Standardization) 12185 test method. The EN 14214 sets the density at 15 °C at 900 kg/m³.

2.3.5. Elemental Analysis

The content in carbon, hydrogen, nitrogen, sulfur and oxygen in rapeseed and sunflower biodiesel and diesel fuel has been measured by Thermo Scientific Flash 2000 CHNS/O, Germany.

2.3.6. Fatty Free Acid Composition of Rapeseed and Sunflower Biodiesel

Fatty free methyl acid composition in rapeseed and sunflower biodiesel has been evaluated by gas chromatography using an FID detector. The samples were collected from the separation funnel (see Figure 1), and prior to being analyzed, were washed with water containing 1% acetic acid and distilled water to neutralized unreacted residues of catalysts, removing side products. The following set up has been used: capillary column $30 \times 0.31 \times 0.25$; helium as gas carrier, flow rate of 1 mL/min; temperature injection 280 °C; temperature detector 300 °C; and temperature ramp 10 °C /min starting from 220 °C.

The total FAME was calculated referring to the total mass of the biodiesel using the following equation

$$FAME (\%) = \frac{\sum m}{b} \times 100$$

where FAME represents the total mass of the fatty acid methyl ester in percentage; the mass of each fatty acid (g) and b the total biodiesel mass (g).

The total content of FAME was compared to the EN 14214 standard.

The measurements were performed in triplicate (Table 1).

Table 1. Total FAME and composition of rapeseed and sunflower biodiesel. The average value with S.D. is reported ($n = 3$).

	Rapeseed Biodiesel	Sunflower Biodiesel	EN 14214
FAME (%)	90.9 (± 1.4)	95.5 (± 1.9)	96.5
Oleic (18:1)	61.2 (± 0.4)	29.4 (± 0.3)	
Linoleic (18:2)	19.7 (± 0.6)	58.3 (± 1.1)	
Linolenic (18:3)	5.1 (± 0.1)	0.8 (± 0.3)	
Palmitic (16: 0)	3.3 (± 0.1)	4.9 (± 0.1)	
Stearic (18:0)	0.9 (± 0.1)	1.4 (± 0.1)	
others	0.7 (± 0.1)	0.6 (± 0.1)	

2.3.7. Oxidation Stability

The oxidation stability was measured by PetroOXY (Petrotest) following the procedure described elsewhere [26]. In brief, 5 cm³ of the sample was placed in the reaction vessel pressurized with oxygen at 700 kPa, and heated to 140 °C. During the oxidation, oxygen is consumed with a subsequent drop in the pressure drop. The variation in the pressure is recorded every second. The elapsed time from the start to the breakpoint is the induction period at the test temperature of 140 °C.

To enhance the oxidation stability of the produced biodiesel, two stabilizers have been tested: 4-allyl-2,6-dimethoxyphenol; and catechol. The effect of the type of stabilizer and the concentration (0.05, 0.1 and 0.3% m/m) on the oil stability were investigated.

3. Results and Discussion

3.1. Effect of the Alcohol Type and Molar Ratio on the Transesterification Yield

In this study, the biodiesel fuels were obtained by transesterification of refined rapeseed and sunflower oils using KOH as a catalyst in methanol or ethanol. The effect of alcohol to molar ratio and the nature of alcohol on the biodiesel yield are resumed in Figure 2. As can be seen, the yield of biodiesel increases with the increase in the concentration of alcohol, and the highest yield was observed at molar ratio of 15:1 and 18:1 for both alcohols, in rapeseed and sunflower oil, respectively. Further increments in the concentration of alcohol led to a decrease in the biodiesel's yield from both oil sources, and particularly using methanol.

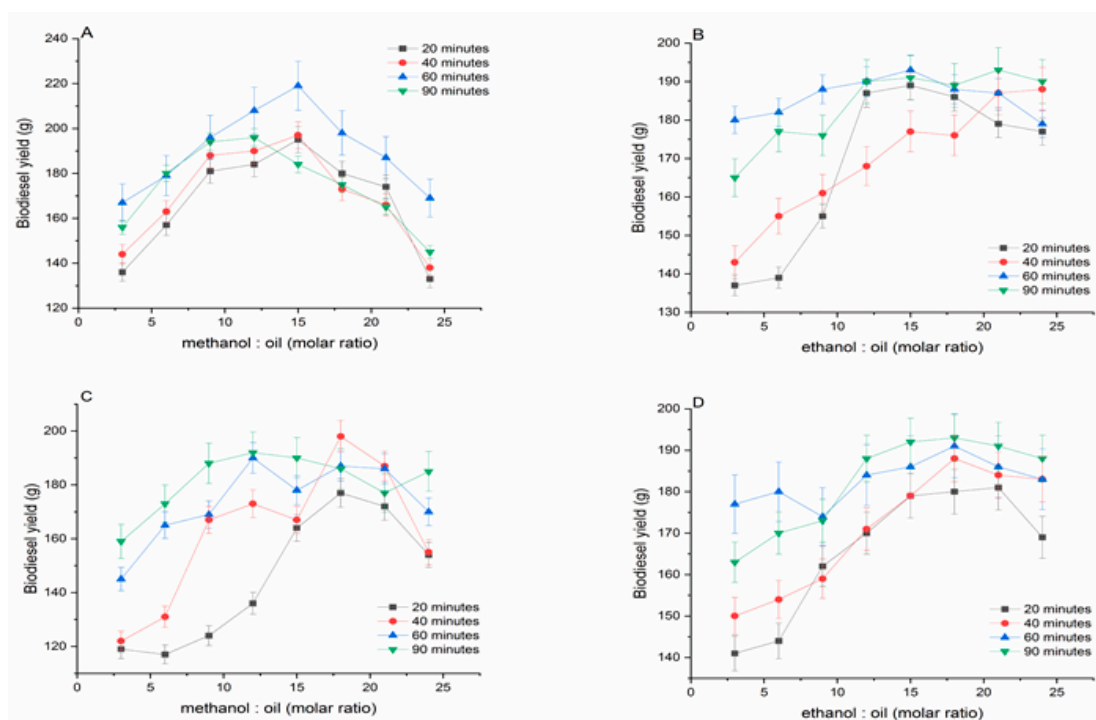


Figure 2. Correlation between the biodiesel yield (g) and the molar ratio of alcohol:oil. (A,B) rapeseed oil; and (C,D) sunflower oil. Data are reported as the average \pm SD ($n = 3$).

As reported in [27–29], the relation between the reaction's yield and the alcohol to oil molar ratio is due to the fact that at molar ratios lower than 15:1 (rapeseed oil) and 18:1 (sunflower oil), the transesterification was still incomplete. As a result, rising alcohol concentration enhances the interactions between alcohol molecules and triglycerides due to an increase in miscibility, moving the reaction toward completion. At molar ratios higher than 15:1 (rapeseed oil) and 18:1 (sunflower oil), the yield decreases, as the high alcohol concentration leads to an increase in glycerol solubility. The increase of the co-product solubility let it remain in the biodiesel phase shift in the reaction equilibrium to the left, and consequently lowers the biodiesel yield. It was observed either with methanol or ethanol, and in both types of vegetable oils. Considering the transesterification conditions tested in the present study, methanol was more reactive with rapeseed and sunflower oils compared to ethanol, as it (methanol) reacts quickly with triglycerides due to its short-chain molar size avoiding the steric hindrance effects and water absorption from atmosphere during transesterification, which directly affect the final yield [28].

Beside the impact of the alcohol: oil molar ratio on the reaction yield, the effect of the reaction time and temperature have been considered (Figure 2).

The temperature influences the reaction rate and the formation of methyl esters (methanol) or ethyl esters (ethanol). In addition, the reaction was carried out at (50 °C) and at atmospheric pressure, to reduce the evaporation of the alcohols. As reported in [30,31], at higher temperatures, an adverse effect could occur. As can be seen in Figure 2, for rapeseed biodiesel, using methanol, the yield tends to increase, with the reaction time reaching the maximum at 60 min, followed by a decrease, while using ethanol, the maximum yield is reached after 60 min, and then tends to be stable. In sunflower biodiesel, the maximum yields are slightly shifted; using methanol, it increases up to 40 min and then decreases, while using ethanol, the maximum yield is reached after 90 min of reaction.

The reduction in the yield when the reaction time is prolonged is probably due to the formation of soaps. As illustrated in Figure 2, the difference in yield is observable depending on the oil feedstock and the alcohol used. Using methanol, there is a decrease in the yield when reaction time is prolonged, while with ethanol it is stable, indicating a probable higher formation of soaps when methanol is used.

3.2. Density

The biodiesel density provides prediction of engine output power and fuel consumption [32,33]. It is generally higher than in fossil fuels, and depends on the composition in fatty acids and the purity of the feedstock. For rapeseed biodiesel, density at 15 °C falls in the range of 0.876–0.891 g/cm³ at the optimal preparation condition (methanol/ethanol to oil molar ratio of 15:1, reaction time of 60 min at 50 °C), while for that of sunflower oil at the same temperature was in the 0.851–0.883 g/cm³ range (methanol/ethanol to oil molar ratio of 18:1, reaction time of 40 min at 50 °C). Considering this, the acceptable range for the standard EN 14214, in which it is reported at 15 °C, is 0.860–0.900 gm/cm³.

3.3. Kinematic Viscosity

Viscosity is an important property to identify and control, as it affects the engine start properties and fuel injection system performance. The fuel-air mix affects the performance of the fuel burning process in a diesel engine. The quality of this mixture depends on the fluidity of the fuel, which is directly linked to the viscosity. The kinematic viscosity at 40 °C is the parameter required by the biodiesel and oil diesel standard. In Figure 3, the kinematic viscosity values of rapeseed and sunflower produced, obtained at different alcohol levels:molar oil levels at different percentage levels, are shown. From Figure 3, the values of kinematic viscosity decrease when the molar ratio increases, reaching the minimum at a molar ratio of 15:1, and then slightly rises. Such a trend is observable at all tested shear rates. The lowest kinematic viscosity values have been observed at share rate of 15·s⁻¹ at a molar ratio of 15:1. A similar trend is observed in sunflower biodiesel, where the lowest kinematic viscosity is observed at alcohol:oil molar ratios of 12:1 (methanol) and 15:1 (ethanol), and a shear rate of 15 s⁻¹.

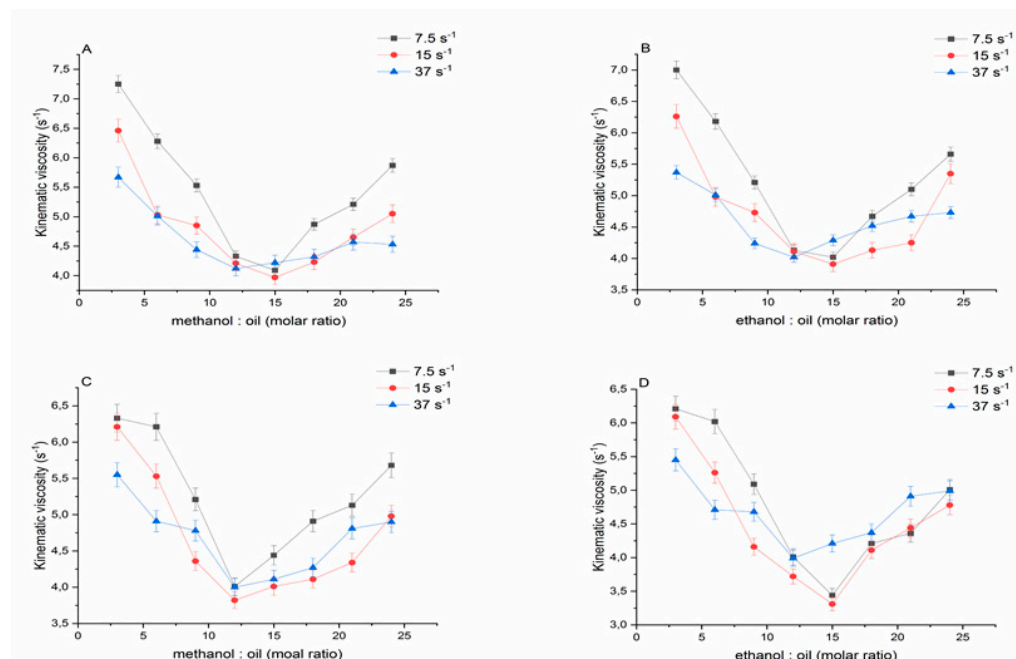


Figure 3. Kinematic -viscosity (40 °C, mm²/s²) of rapeseed biodiesel obtained using methanol (A) and ethanol (B), and sunflower biodiesel obtained using methanol (C) and ethanol (D) at a different alcohol to oil molar ratio. Data are reported as the average ± SD (*n* = 3).

The large differences between the viscosity of rapeseed and sunflower oil and the respective biodiesel is due to the conversion of large and branched triglyceride molecules into a lighter linear chain of methyl or ethyl ester molecules. This finding shows that the trans-esterification process has considerably improved the viscosity property of rapeseed and sunflower oil, reaching a value comparable to that of mineral diesel. This viscosity differential can be used to control biodiesel production through transesterification [34].

3.4. Higher Heating Value (HHV)

The higher heating value (HHV) is defined as a thermal energy released by the combustion of a unit quantity of fuel, and hence characterizes the energy content of the fuel [35,36]. HHV measurements of colza and sunflower biodiesel obtained with methanol and ethanol at different molar ratios are given in Figure 4. The HHV of the biodiesel samples is relatively high, ranging in the case of rapeseed biodiesel from 39.24 to 41.18 MJ/kg and from 38.58 to 41.07 MJ/Kg obtained using methanol and ethanol, respectively. In biodiesel from sunflower, the values range from 36.92 to 40.69 MJ/Kg (methanol) and 38.92 and 39.60 MJ/Kg (ethanol). Although these values fall within the required standards, they are slightly lower compared to fossil diesel. This result can be explained by the presence of oxygen in the biodiesel, as well as by the low percentage of carbon and hydrogen compared to fossil diesel (see Table 2 elemental analysis). It can be emphasized that data are very spare because of no regular increase or decrease tendency when the molar ratio is increased. The rapeseed biodiesel has its maximum heating value at 15:1 (using methanol) and 21:1 (using ethanol), while sunflower biodiesel shows the highest HHV at 18:1 (using methanol) and 24:1 (using ethanol).

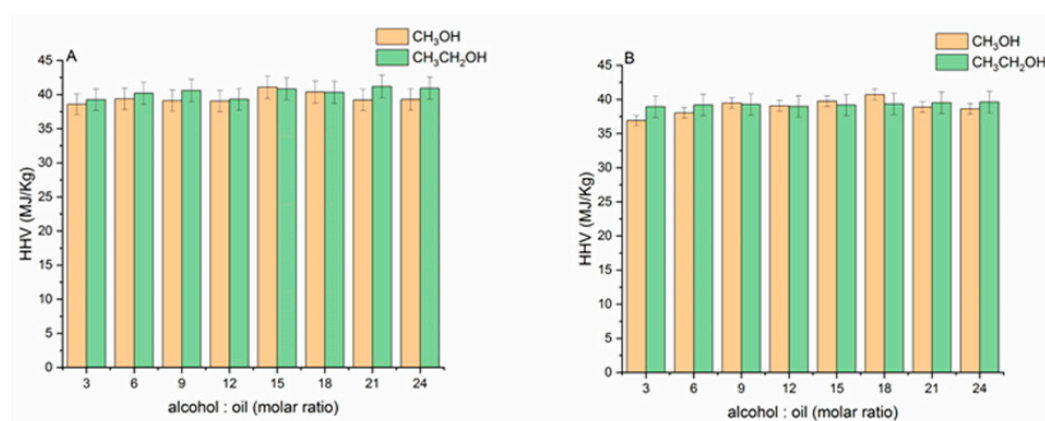


Figure 4. HHV of biodiesel obtained at various alcohol: oil molar ratio. (A) rapeseed biodiesel and (B) sunflower biodiesel. Data are reported as the average \pm SD ($n = 3$).

Table 2. Elemental analysis of SB (biodiesel from sunflower oil); RB (biodiesel from rapeseed oil) and diesel. Both were obtained using methanol. Measurements were performed in triplicate, and the average value is reported. S.D. less than 5% ($n = 3$).

Element	SB	RB	Diesel
C	80.3	79.9	86.6
H	10.5	10.3	13.4
O	8.1	8.5	-
N	1.1	1.3	-
C/H	7.6	7.7	6.46

3.5. Flash Point

The flash point is the lowest temperature at which a fuel releases a sufficient concentration of vapors that have mixed with air and become inflamed [25]. The flash point temperature indicates the overall flammability hazard in the presence of air; a higher flash point makes bio-diesel safer for handling and storing, and for this reason, knowing the flash point is fundamental for every type of biodiesel in order to classify it as nonhazardous under the fire regulations. Compared to diesel, biodiesel has a higher flash point due to the presence of fatty acid methyl esters (FAMES) or fatty acid ethyl esters (FAEEs), which are not volatile. As the flash point varies inversely with the fuel's volatility, biodiesel is safer to handle at a higher temperature than fossil diesel.

The flashpoint of the rapeseed (RB) and sunflower (SB) biodiesel pure and in the blend with diesel was evaluated, and the results are resumed in Figure 5. The biodiesel–diesel blends were prepared by mixing the two components at a different weight ratio.

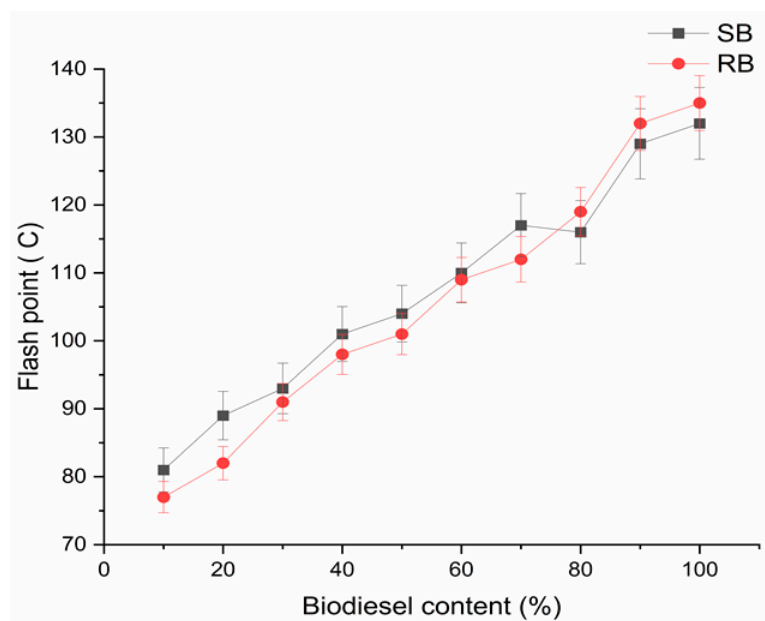


Figure 5. Relationship between flash point (°C) and biodiesel content in the biodiesel–diesel mixture. SB = sunflower biodiesel; RB = rapeseed biodiesel. Both were obtained using methanol at the optimal molar ratio, as described in the previous sections.

The biodiesels used for the flash point characterization were: (1) from rapeseed oil, biodiesel obtained at alcohol: oil molar ratio of 15:1, 60 min reaction time at 50 °C; and (2) from sunflower that obtained at 18:1 molar ratio; 40 min reaction time and 50 °C.

The flash point values can vary according to the source and the quality of the oil [37].

The trends in Figure 5 show that the highest flashpoint for pure BS and RB are similar without a statistical difference. In the case of biodiesel–diesel blends, as expected and reported in several published works [38], increasing the percentage of diesel in the blend biodiesel–diesel causes the flash point temperature decrease, reaching the lowest value at around 80 °C for SB and RB (10% biodiesel–90% diesel) (This is due to the fact that diesel has a lower flashpoint compared to biodiesel, and thus the resulting blend (diesel–biodiesel) has a lower flashpoint than the pure biodiesel. The reduction in the flashpoint value is proportional to the percentage of diesel in the blend. As a general conclusion, no statistical differences have been observed in the SB and RB flash point vs. biodiesel content as the trends overlap.

3.6. Elemental Analysis of Biodiesels and Diesel

In Table 3, the C, H, O, N content in biodiesel from sunflower oil (SB) and rapeseed oil (RB) are reported and compared to the fossil fuel diesel.

The elemental analysis demonstrates no significant difference in the C, H, O, N content between SB and RB. Compared to diesel, however, the C and H content in SB and RB is slightly lower, as also demonstrated in previous studies [39,40], with a consequent increase in the C/H ratio.

One key difference between biodiesel fuels and petroleum diesel is the high content of oxygen, which improves combustion and performance characteristics. Biodiesel has a small nitrogen content, which results in higher emissions of NO_x.

Table 3. Oxidation stability of the biodiesel and its blends with additives: results for 4-allyl-2,6-dimethoxyphenol (All) and catechol (Cat), blended with sunflower and rapeseed biodiesel. SB and RB were both obtained using methanol at the appropriate molar ratio.

	Additive Content (% m/m)		PetroOXY (min)	
Sunflower Biodiesel (SB)	-	-	9.08	
	0.05 (All)	0.05 (Cat)	11.03 (All)	29.57 (Cat)
	0.1 (All)	0.1 (Cat)	17.39 (All)	41.05 (Cat)
	0.3 (All)	0.3 (Cat)	28.55 (All)	58.55 (Cat)
Rapeseed Biodiesel (RB)	-	-	15.91	
	0.05 (All)	0.05 (Cat)	23.19 (All)	32.58 (Cat)
	0.1 (All)	0.1 (Cat)	29.67 (All)	49.67 (Cat)
	0.3 (All)	0.3 (Cat)	41.11 (All)	59.13 (Cat)

3.7. Biodiesel Oxidation Stability and Effect of Stabilizers

Oxidation stability is a physical property, which describes the ageing behavior of liquid fuels during transport and storage. In biodiesel and its blends with diesel, oxidation can cause the formation of acid and solids, which can cause several issues at the supply system due to deposition. Herein, the oxidation stability has been evaluated using the PetroOXY test chamber. A 5 mL fuel sample is combined with 700 kPa oxygen and heated to 140 degrees Celsius. This initiates a fast oxidation, whose results are determined by the time needed to achieve a pressure drop of 10% in the system. Testing confirmed that the time needed to achieve the 10% drop in pressure is directly related to the sample's oxidation stability.

The effect of two well-known and widely used additives, 4-allyl-2,6-dimethoxyphenol and catechol, on the oxidation stability, has also been evaluated.

Consistent with the results of previous studies, additives have an effect on the oxidative stability of both types of biodiesel [41–43]. It should be noted that despite the very small amounts of additives added, these compounds significantly improve oxidation stability, particularly in catechol.

The additives tested in this work affect the oxidation stability of the bio-diesel samples of sunflower and rapeseed. Their effect is more intense with higher percentages added to the biodiesel. In Figure 6, the oxidation stability measurements conducted with the PetroOXY method vs. the concentration of additive for both biodiesel samples are reported. As can be seen, oxidation stability has the maximum value in BS or RB when the greatest amount of catechol has been added to 0.3% (m/m). According to the results of previous studies, additives affect the oxidation stability of both types of biodiesel [41–43]. It is worth bearing in mind that if the added amount is too high, the use of additives could produce a negative effect on the oxidation stability of the biodiesel [44,45]. The results indicate that catechol as an additive provides the best performance either in sunflower or in rapeseed biodiesel. The use of catechol as an additive blended with rapeseed and sunflower biodiesel, even in very small amounts as low as 0.05% mass fraction, enables the restrictive limit imposed by the EN14214 standard to be complied with. However, the pure biodiesel is far from meeting the threshold value. The addition of catechol to rapeseed biodiesel in amounts as low as 0.10% mass fraction enables compliance with the EN14214 standard. With regards to 4-allyl-2,6-dimethoxyphenol, its use would only be satisfactory in the case of the rapeseed biodiesel blended with additive contents above 0.3% mass fraction.

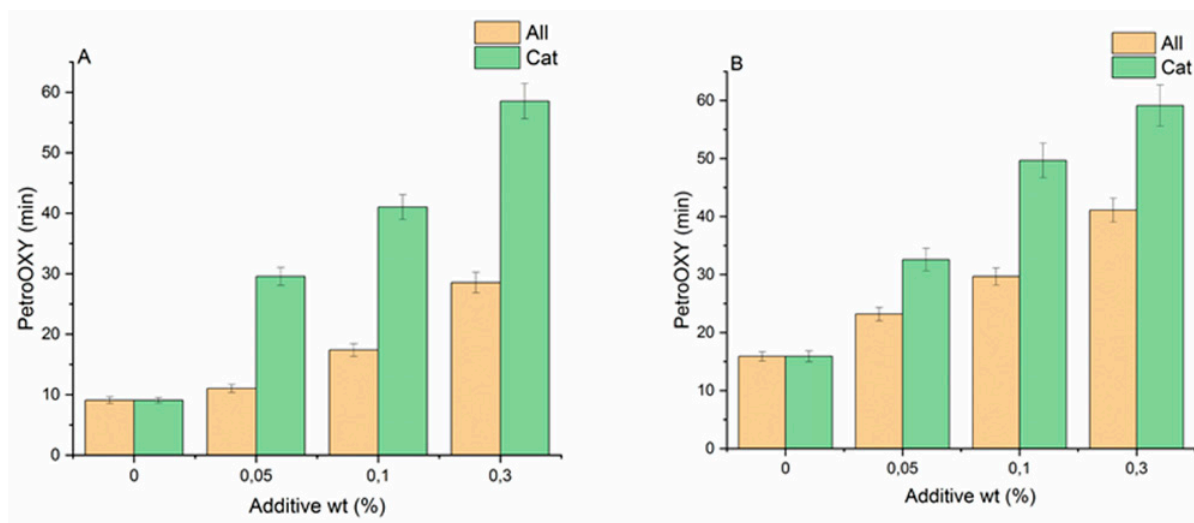


Figure 6. Variation of PetroOXY induction time (min) for rapeseed biodiesel (A) and sunflower biodiesel (B) without and in the presence of two additives (All = 4-allyl-2,6-dimethoxyphenol; Cat = catechol).

4. Conclusions

Biodiesel is a promising alternative to oil because of its ecological and renewable nature. Transesterification represents the most-used approach for biodiesel production, and depends on various parameters, including the type of alcohol used and the molar ratio (alcohol:oil), the catalyst and its concentration, the temperature and the reaction time. The production method is key to efficient and profitable biodiesel production. In the present study, we reveal that the optimum reaction conditions using rapeseed oil and KOH catalyst were an alcohol:oil molar ratio of 15:1, a 60-min reaction time at 50 °C; while in the case of sunflower oil, the best yield and biodiesel quality were at a 18:1 molar ratio, a 40 min reaction time and 50 °C.

Moreover, the oxidation stability of biodiesel can greatly be improved by adding up to 0.3% m/m catechol, which increases the protoOXY to 60 min.

The set up condition results in the highest biodiesel yield, and the products meet the required standards, and are similar to mineral diesel with the same requirements.

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